Dependence of Concentrations of Phases on the Amplitude of the External Field in the Domain of Metastability of Both Phases.

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Abstract

In this study we analyzed kinetics of phase concentrations in the electrically loaded systems in the region where both phases are metastable simultaneously. We determined the dependence of the equilibrium concentration of phases upon the amplitude of the external electric field, and demonstrated a feasibility to control the equilibrium concentration of the phases by changing the amplitude of the external electric field .

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1. Introduction

In our previous studies [1-4] we investigated peculiarities of phase transitions in current caring conductor when these transitions are accompanied by a sharp change of electric conductivity. It was shown that ponderomotive forces prevent from formation of the nuclei with the electric conductivity lower than that of the surrounding medium, and promote nucleation when the electric conductivity of a nucleus is higher than that of a surrounding medium. This mechanism results in a number of different effects and, in particular, the existence of the domain where both phases are metastable. Clearly, the kinetics of the concentrations of phases in this domain must be different than that in the common situation where one phase is stable and other is metastable. In this study we investigated the kinetics of the concentration of phases in the domain of their metastability.

In addition to the case of the current-carrying conductors we investigate also the effect of the electrostatic field on the kinetics of the phase transitions occurring in dielectrics.

Using the results that was derived in our previous studies [1-4] we can write the condition of the phase equilibrium between two phases in the electrically loaded system. Hereafter the parameters of the external phase (the host medium) are denoted by a subscript "0" and the parameters of the internal phase (nucleus) are denoted by subscript "1". The condition of the equilibrium between phases reads:

$$\mu_1(p,T) + v_1(\tilde{p} + p_S) = \mu_0(p,T) \tag{1}$$

where μ_1, μ_0 are chemical potentials of the internal and external phase, correspondingly, v_1 is specific volume of the internal phase, p is external pressure, T is temperature of the system and $\tilde{p}$ is the ponderomotive pressure. In the case of a spherical nucleus the surface tension pressure

$$p_S = \frac{2\alpha}{r_1}.$$

In the case of the phase transition in a current-carrying conductor

$$\tilde{p} = \tilde{p}_m = 2\xi_m p_m \Phi(r_1), \tag{2}$$

where $\xi_m = \dfrac{1-\kappa_\sigma}{2+\kappa_\sigma}$, $p_m = \dfrac{I^2}{\pi\rho_0{}^2 c^2}$, I is a total electric current passing through the conductor, ρ_0 is a radius of the cylindrical conductor , c is a speed of light, $\kappa_\sigma = \dfrac{\sigma_1}{\sigma_0}$, σ_1 and σ_0 are electric conductivities of the nuclear and of the host medium, respectively, $\Phi(r_1)$ is a geometric factor that depends upon the distance between the surface of the conductor and the center mass of the nuclear .

In the case when phase transition occurs in the dielectric in the presence of the external electric field

$$\tilde{p} = \tilde{p}_E = \frac{3\varepsilon_0 E^2 \xi_\varepsilon}{8\pi}, \quad \xi_\varepsilon = \frac{1-\kappa_\varepsilon}{\kappa_\varepsilon + 2}, \quad \kappa_\varepsilon = \frac{\varepsilon_1}{\varepsilon_0}, \tag{3}$$

where E_0 is the strength of the electric field, ε_0, ε_1 are dielectric permitivities of the external (host) and of the internal (nucleus) phases, respectively.

Further analysis is performed using Eq. (1) in order to determine the size of the critical nucleus r_- for a phase transition $+ \to -$ and r_+ for a phase transition $- \to +$. Hereafter subscripts $+$ and $-$ denote a high temperature and a low temperature phases, respectively. Using Eq. (1) in the vicinity of the temperature $T = T_0(p)$ for a given pressure p we find that for a phase transition $+ \to -$ (phase $-$ is considered to be internal):

$$r_-(T) = -\frac{2\alpha v_-^0}{\lambda_0 \dfrac{\Delta T}{T_0} + v_-^0 \tilde{p}_-}, \quad \Delta T = T - T_0 \tag{4}$$

where v_-^0 is a specific volume of a low temperature phase at the phase equilibrium curve $T = T_0(p)$, the latent heat of a phase transition $\lambda_0 = T_0\left(s_+^0 - s_-^0\right) > 0$, s_+^0 and s_-^0, are specific entropies of high temperature and low temperature phases, respectively, $\tilde{p}_-$ is determined by the formulas (2) or (3) and subscript "1" denotes the low temperature phase and subscript "0" denotes the high temperature phase. Similarly we can consider a phase transition $- \to +$, and assuming that internal phase is a high temperature phase we arrive at the following formula for the radius of the critical nucleus:

$$r_+(T) = \frac{2\alpha v_+^0}{\lambda_0 \frac{\Delta T}{T_0} - v_+^0 \tilde{p}_+}, \tag{5}$$

where v_+^0 is a specific volume of the high temperature phase.

Eq. (4) allows us to determine a temperature T_- such that at temperatures $T > T_-$ the nuclei of the low temperature phase ($-$) are not formed:

$$\frac{T_- - T_0}{T_0} = -\frac{v_- \tilde{p}_-}{\lambda_0}, \tag{6}$$

while Eq. (5) allows us to determine a temperature T_+ such that at temperatures $T < T_+$ the nuclei of the high temperature phase $+$ are not formed:

$$\frac{T_+ - T_0}{T_0} = \frac{v_+ \tilde{p}_+}{\lambda_0}. \tag{7}$$

Let us introduce a parameter

$$\gamma = \frac{T_- - T_0}{T_+ - T_0}.$$

In the case of the phase transition in the current caring conductor this parameter is determined by the following equation:

$$\gamma = \gamma_\sigma = \frac{v_-}{v_+} \frac{(1 + 2\bar{\kappa}_\sigma)}{(\bar{\kappa}_\sigma + 2)}, \quad \bar{\kappa}_\sigma = \frac{\sigma_-}{\sigma_+} \tag{8}$$

In the case of the phase transition of the first kind in the dielectric in the external electric field this parameter is given by the following expression:

$$\gamma = \gamma_\varepsilon = \frac{1+2\bar{\kappa}_\varepsilon}{(\bar{\kappa}_\varepsilon+2)\bar{\kappa}_\varepsilon}\frac{v_-}{v_+} > 0, \quad \bar{\kappa}_\varepsilon = \frac{\varepsilon_-}{\varepsilon_+}. \tag{9}$$

Eqs. (8), (9) imply that the curves $T_-(p)$ and $T_+(p)$ are shifted in the same direction with respect to the curve $T_0(p)$ since the differences $T_- - T_0$ and $T_+ - T_0$ have the same sign. As follows from Eqs. (4)-(7) when $\kappa > 1$* the curves $T_-(p)$ and $T_+(p)$ are shifted towards higher temperatures, and when $\kappa < 1$ these curves are shifted towards lower temperatures.

If $T_-(p) < T_+(p)$, then in the temperature range

$$T_-(p) < T < T_+(p) \tag{10}$$

the nuclei of the new phase are not formed. The latter conclusion is a direct consequence of the definition of $T_-(p)$ and $T_+(p)$. In the temperatures range (10) both phases are stable, i.e., it is a range of a hysteresis. Occurrence of a particular phase in this domain depends upon the direction of the process. Thus, heating retains a low temperature phase while cooling retains a high temperature phase. When $\kappa > 1$, the temperatures range (10) is determined by a condition $\gamma < 1$ while for $\kappa < 1$ the range of hysteresis is determined by a condition $\gamma > 1$.

A different situation occurs when $T_+(p) < T_-(p)$. In the latter case in the temperature range

$$T_+(p) < T < T_-(p) \tag{11}$$

both phases are metastable, so that the radii of the critical nuclei for the direct and inverse phase transitions, $r_+(T)$ and $r_-(T)$, assume finite positive values. The latter can be verified as follows. Eliminating $\Delta T/T_0$ in formulas (4), (5) we find that

$$\frac{2\alpha v_+}{r_+} + \frac{2\alpha v_-}{r_-} = -v_-\tilde{p}_-\frac{\gamma-1}{\gamma} = v_+\tilde{p}_+(\gamma-1). \tag{12}$$

In the domain where both phases are metastable, $r_+(T)$ and $r_-(T)$ assume positive and finite values. Eq. (12) implies that such situation can occur only when its right-hand side is

* Hereafter we will use a notation κ when exposition is the same for κ_ε and κ_σ.

positive. Since for $\kappa > 1$, $\tilde{p}_- > 0$ and $\tilde{p}_+ < 0$, Eq. (12) implies that a condition for metastability of both phases in the range $\kappa > 1$ is $\gamma > 1$. Similarly it can be showed that in the range $\kappa < 1$ the condition for metastability of both phases is $\gamma < 1$. In this case a condition (11) again corresponds to the condition metastability of both phases.

In Figs. 1-2 we showed locations of the different domains of stability of phases for $\kappa > 1$ and $\kappa < 1$ on the temperature axis. In Fig. 3 we showed locations of the domains of metastability of both phases on $v_-/v_+, \varepsilon_-/\varepsilon_+$ plane in the case of the phase transition in the dielectric in the presence of external electric field. In Fig. 4 we showed locations of the domains of metastability of both phases on $v_-/v_+, \sigma_-/\sigma_+$ plane in the case of the phase transition in a current-caring conductor.

Above we considered different thermodynamic regions at the temperature axis for a given magnitude of pressure. Similarly we can use Eq.(1) to analyze different thermodynamic regions at the pressure axis for a given magnitude of temperature. Expanding Eq. (1) in the vicinity of the curve $p = p_0(T)$ and using considerations similar to those employed in the analysis of the temperatures range we arrive at the thermodynamic domains of stability of phases shown in Figs. 1, 2, where the parameters p_-, p_+ are defined similarly to the parameters T_-, T_+, i.e. for $p > p_-$ a low pressure phase is not formed , and for $p < p_+$ a high pressure phase is not formed.

In conclusion let us consider kinetics of formation of two phases. Let x_+ and x_- are concentrations of a high temperature and a low temperature phases, respectively. We neglect fluctuations of concentrations and consider a linear domain where concentrations of both phases are far from the depletion. Let p_+ and p_- be probabilities of formation of phases (see [5], Chapter 12 , Section 99). Since $x_+ + x_- = 1$ using the local approximation we find that

$$\dot{x}_+ = p_+(1 - x_+) - p_- x_+ ,$$

or

$$x_+(t) = \frac{\varphi}{1+\varphi} + \exp(-\gamma t)\left(x_+(0) - \frac{\varphi}{1+\varphi} \right), \quad \varphi = \frac{p_+}{p_-},$$
$$x_-(t) = \frac{1}{1+\varphi} + \exp(-\gamma t)\left(x_-(0) - \frac{1}{1+\varphi} \right).$$

In the linear region where both phases are far from depletion the probability of phase formation is determined by the radii of the critical nuclei (see [5], Chapter 12, Section 99), $p_{\pm} \propto \exp\left(-4\pi\alpha r_{\pm}^2/3kT\right)$, and

$$\varphi = \exp\left[-\frac{4\pi\alpha\left(r_+^2 - r_-^2\right)}{3kT}\right]. \tag{13}$$

Here r_+ and r_- are sizes of the critical nuclei of the phases in the domain of coexistence of phases which were determined above. Substituting these values into formula (13) yields the dependencies of phase concentrations x_+ and x_- upon the amplitude of the external electric field.

In the following we consider phase transitions in a dielectric medium separately from phase transitions in a current-carrying conductor. Direct substitution of Eqs. (4)-(5) into Eq. (13) yields expression which is too cumbersome for the direct analysis. In order to derive simple formulas for the dependencies of concentrations of phases on the amplitude of the external electric field let us define the electric field

$$E_e^2 = \frac{\Delta T}{T_0}\frac{\lambda_0}{\tilde{V}(\kappa)}, \tag{14}$$

where $\tilde{V}(\kappa) = \frac{v_- v_+}{v_+ + v_-}\frac{\kappa - 1}{8\pi}\beta_+ \frac{3\left(\kappa^2 + 4\kappa + 1\right)}{(\kappa + 2)(1 + 2\kappa)}, \quad \kappa = \overline{\kappa}_\varepsilon$.

When the external electric field $E_0 = E_e$, then at a given ΔT, $r_+(T) = r_-(T)$, i.e., $\varphi = 1$. Thus, formula (14) determines the magnitude of the external electric field E_e that renders concentrations of both phases equal. Now let us determine the dependence of the ratio of concentrations of phases $\varphi = x_+(\infty)/x_-(\infty)$ in the vicinity of $\varphi = 1$ upon the magnitude of the external electric field. Formulas for the sizes of the nuclei can be rewritten as follows:

$$r_-(T) = \frac{r_*}{1 - \frac{\left(x^2 - 1\right)A}{1 - A}}, \quad r_+(T) = \frac{r_*}{1 + \frac{\left(x^2 - 1\right)A}{A - s\tau}}, \tag{15}$$

where r_* is a radius of the critical nucleus for $\varphi = 1$

$$r_* = \frac{r_1^0}{1 - A} = \frac{r_1^0 \tau}{A - \tau s}\ , \tag{16}$$

r_1^0 is a radius of the critical nucleus without external electric field for a given temperature difference ΔT :

$$r_1^0 = \frac{2\alpha v_1}{\lambda_0 \frac{|\Delta T|}{T_0}}$$

and

$$s = v_- / v_+, \quad \tau = \frac{1 + 2\kappa}{\kappa(\kappa + 2)}, \quad A = \frac{\tau(1+s)}{1+\tau}. \tag{17}$$

The magnitudes of parameters A, s and τ are determined by the characteristics of phases. Thus, Eqs. (15), (16) determine the range of the external electric field E_0 where both phases are metastable. This range of the external electric field can be found from the conditions that sizes of the critical nuclei of both phases are positive, i.e., $r_-(T) > 0$ and $r_+(T) > 0$. The latter conditions yield

$$\frac{\Delta T}{T_0} \frac{\lambda_0}{\tilde{V}(\kappa)} \frac{s(1+\tau)}{1+s} < E_0^2 < \frac{\Delta T}{T_0} \frac{\lambda_0}{\tilde{V}(\kappa)} \frac{1+\tau}{\tau(1+s)}. \tag{18}$$

Note that a condition $r_* > 0$ or $\tau s < A < 1$, is a particular case of the Eq. (18) at $E_0 = E_{e\pm}$ Using Eqs (13) ,(15) we arrive at the following formula for the ratio of concentrations of two phases:

$$\ell n(\varphi) = \frac{4\pi\alpha r_0^2}{3kT} \frac{\left[2\xi\tau + \xi^2(1-\tau)\right](1+\tau)}{(1-\xi)^2(\tau+\xi)^2(1-A)^2}, \tag{19}$$

where $\xi = \dfrac{E_0^2 - E_e^2}{E_e^2}\dfrac{A}{1-A}$.

Eq. (19) determine the dependence of the ratio of concentrations of both phases on the magnitude of the applied electric field and parameters of the problem.

Similarly we can investigate the case of the phase transitions in a current-carrying conductor. In the following we present only final results. Similarly to the amplitude of the external electric field given by Eq. (14) let us introduce the magnitude of the electric current I_e:

$$\frac{I_e^2}{\pi\rho_0^2 c^2} = \frac{\Delta T}{T_0}\frac{\lambda_0}{\tilde{V}_i(\kappa)}, \quad \tilde{V}_i = \frac{6v_- v_+(\kappa^2-1)}{(v_+ + v_-)(1+2\kappa)(\kappa+2)}, \quad \kappa = \overline{\kappa}_\sigma = \frac{\sigma_-}{\sigma_+} \quad . \tag{20}$$

When the magnitude of the electric current passing through the conductor $I = I_e$, then for a given temperature difference ΔT, $r_+(T) = r_-(T)$, i.e., $\varphi = 1$. Thus formula (20) determines the magnitude of the electric current that renders concentrations of the both phases equal. Using this equation, and formulas (2),(4),(5) we can derive equations similar to Eqs. (15)-(17) with the only difference that a parameter τ is defined as follows:

$$\tau = \tau_i = \frac{1 + 2\overline{\kappa}_\sigma}{\overline{\kappa}_\sigma + 2}$$

The range of the magnitudes of the electric current where both phases metastable is determined by the following equation:

$$\frac{\Delta T}{T_0}\frac{\lambda_0}{\tilde{V}_i(\kappa)}\frac{s(1+\tau_i)}{1+s} < p_e < \frac{\Delta T}{T_0}\frac{\lambda_0}{\tilde{V}_i(\kappa)}\frac{1+\tau_i}{\tau_i(1+s)}, \quad p_e = \frac{I_e^2}{\pi\rho_0^2 c^2},$$

and the ratio of the concentrations of phases is determined by Eq. (19) where

$$\xi = \xi_i = \frac{I^2 - I_e^2}{I_e^2}\frac{A_i}{1-A_i}$$

and A_i is determined by Eq. (17) with $\tau = \tau_i$.

4. Discussion

The main result that was obtained in this study is that we demonstrated the feasibility to control concentrations of phases in the system by varying the amplitude of the electric current or the external electrostatic field. The feasibility to control concentrations of phases arises in the systems that are subjected to the external electromagnetic field due to the existence of the domain where both phases are metastable. The main impediment to the observation of the effects considered in this investigation is that even for the large electric currents or electric fields the magnitude of the shift of the temperature of the phase transition due to the influence of the electric field, $\Delta T/T_0$, is small with respect to the range of variation of thermodynamic parameters during phase transition (see Refs. [3], [6]). Therefore the temperature range where the considered effects can be realized, $\Delta T/T_0 \sim \tilde{p} v_0/\lambda_0 << 1$, is very narrow. However this range can be quite large when the latent heat of phase transition is small. The existence of the domain where two phases are metastable can be realized also when other types of external loading are applied. It is reqiured only that the thermodynamic pressure in the system is renormalized, and the magnitude of the renormalized pressure must depend on which phase is the external phase and which phase is the internal phase.

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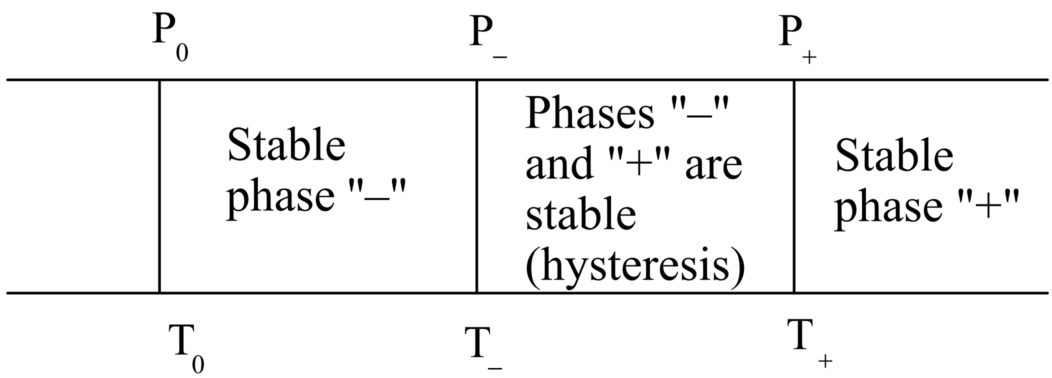
Figures captions

Fig. 1. Location of domains af stability and metastability of pases for different values of parameter γ ($\kappa > 1$).

Fig. 2. Location of domains af stability and metastability of pases for different values of parameter γ ($\kappa < 1$).

Fig. 3. Domains of metastability of both phases on $v_{-}/v_{+}, \varepsilon_{-}/\varepsilon_{+}$ plane.

Fig. 4. Domains of metastability of both phases on $v_{-}/v_{+}, \sigma_{-}/\sigma_{+}$ plane.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P_-
P_+
Stable phase "–"
Phases "–" and "+" are stable (hysteresis)
Stable phase "+"
T_0
T_-
T_+

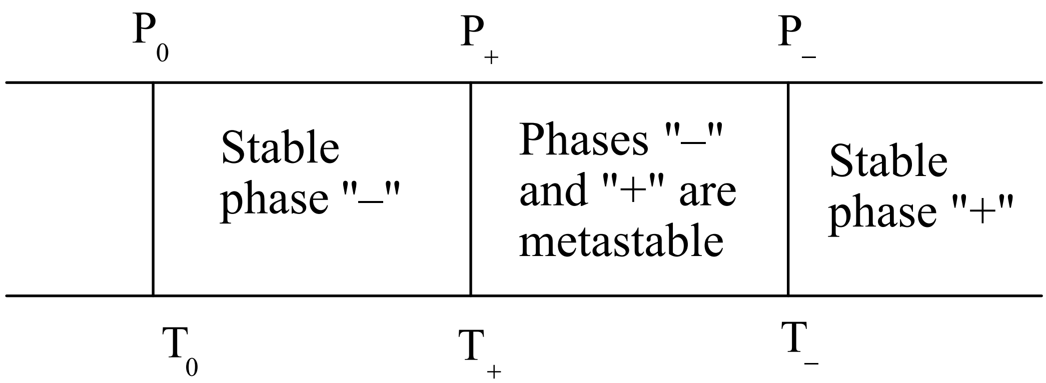
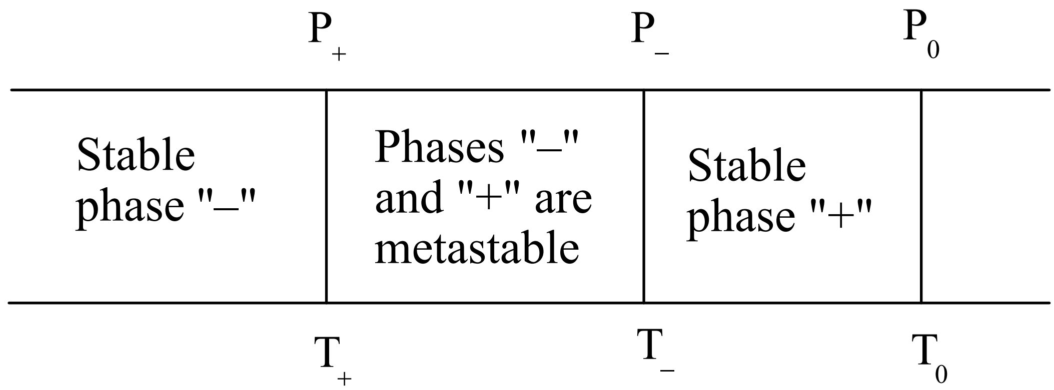

P_0
P_+
P_-
Stable phase "–"
Phases "–" and "+" are metastable
Stable phase "+"
T_0
T_+
T_-

Figure 1, Yu. Dolinsky&T. Elperin, Dependence of concentrations of phases on the amplitude of the external field in the domain of metastability of both phases.



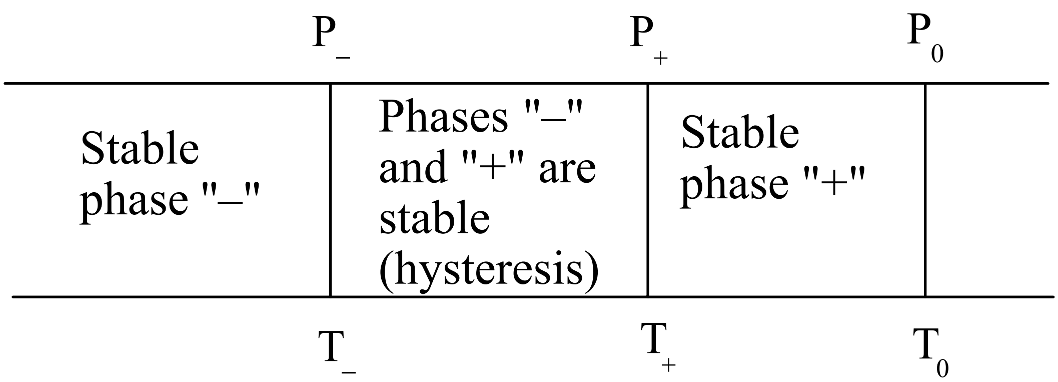


Figure 2, Yu. Dolinsky&T. Elperin, Dependence of concentrations of phases on the amplitude of the external field in the domain of metastability of both phases.

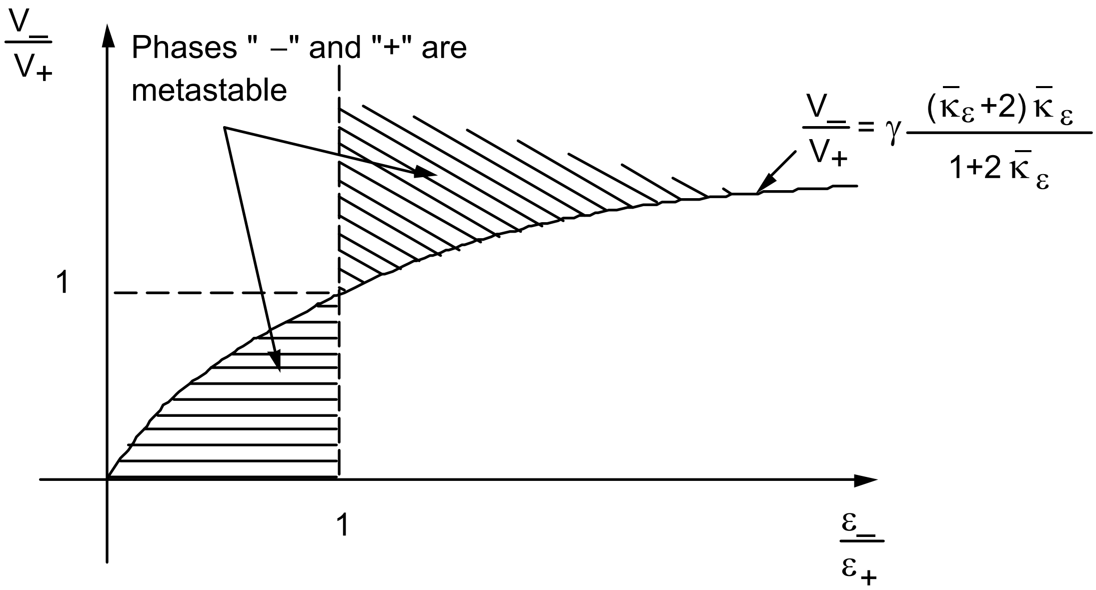


Figure 3, Yu. Dolinsky&T. Elperin, Dependence of concentrations of phases on the amplitude of the external field in the domain of metastability of both phases.

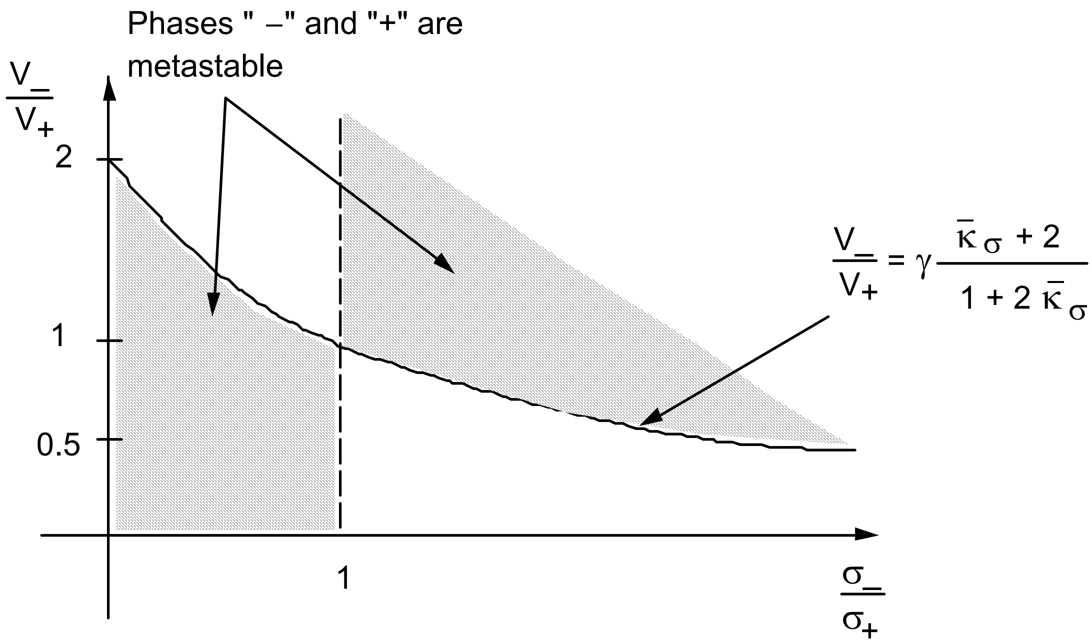


Figure 4, Yu. Dolinsky&T. Elperin, Dependence of concentrations of phases on the amplitude of the external field in the domain of metastability of both phases.